AMENDED SPECIFICATION

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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Cellulosic Material

We, W. & R. BALSTON LIMITED, a British Company, of Springfield Mill, Maidstone, Kent, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for improvements in or relating to cellulosic material and is particularly concerned with the preparation of phosphorus-containing cellulosic material.

It is an object of the present invention to prepare a phosphorus-containing fibrous cellulosic material having selective adsorbent or ion-exchange properties for the purpose of separating mixtures of ions or compounds by preferential selection, e.g. by chromatography, sorption, ion-exchange, complexing, and other separative methods.

According to the present invention there is provided a process for the preparation of a phosphorus-containing cellulosic material having selective adsorbent or ion-exchange properties, which process consists essentially in the impregnation of cellulosic material with an aqueous solution of a phosphorus acid and urea, the aqueous solution containing a relative proportion of nitrogen to phosphorus of at least one atom of nitrogen per atom of phosphorus, the ratio by weight of the solution to cellulose being at least 1.5:1 and the ratio by weight of cellulose to phosphorus acid in the reaction mixture not exceeding 5:1, and heating the impregnated material for at least 20 minutes at a temperature between 120° and 200°C, the heating of the impregnated material being such that the final product contains at least 5.5% by weight of combined phosphorus.

The cellulosic material which is treated in accordance with the present invention is fibrous cellulose of various origins, such as wood cellulose and cotton cellulose, and it may be in thread, web, sheet, pulp, floc or powder form. Preferably the cellulosic material is a very pure grade of chemical wood pulp containing approximately 98 per cent by weight of alpha-cellulose and small quantities of beta- and gamma-cellulose. Other forms of cellulose that may also be used are regenerated cellulose in various physical forms, such as film, filament, web, powder, yarn or sheet form. Non-cellulosic material may be admixed with the cellulosic material, for example, the cellulosic material may be admixed with organic or inorganic fibres such as glass or plastic microfibres, the mixture being preferably in the form of a sheet, web or thread. Reaction of the cellulosic material with the impregnating compound may be facilitated for example by pre-treatment of the cellulosic material such as pre-swelling in alkali in known manner.

The treated cellulose must contain at least 5.5% by weight phosphorus and this is achieved by employing the specified reaction conditions, the liquor present in the cellulose after the impregnation step being such that the cellulose contains sufficient phosphorus acid to be capable of yielding a product containing not less than one combined phosphorus acid group for every three monosaccharide units of the cellulse.

The ratio of phosphorus acid to cellulose

in the steeped cellulose should preferably not exceed 1:1.

In a preferred form of the present invention the solution used to impregnate the cellulosic material consists of,

Orthophosphoric acid	5 to 20% by weight
Urea	10 to 50% by weight
Water	to make up to 100%

In some forms of the present invention the solution may contain up to 35% by weight of orthophosphoric acid, and in others it may contain up to 60% by weight of urea. The ratio by weight of urea to phosphoric acid is preferably greater than 1.5:1.

Other phosphorus acids, e.g. metaphosphoric acid or phosphorous acid, may be employed in place of orthophosphoric acid.

There may be employed in conjunction with the urea other basic nitrogen-containing compounds or their salts, for example guanyl urea sulphate, amino guanidine hydrogen carbonate

$$[(H_2N—NH—C(=NH_2)—NH_2)\ HCO_3],$$

guanidine nitrate, phenyl biguanide, formamide, ammonium phosphate or urea phosphate. The solution used to impregnate the cellulosic material may be a solution of urea phosphate.

The aqueous solution of the acid and urea may be prepared by dissolving the two compounds in hot or cold water or by melting the two compounds together and then dissolving the hot or cooled melt in water.

The impregnation of the sheet cellulosic material may be carried out by steeping it in the phosphorus acid liquor and thereafter removing the excess for example by squeezing or centrifuging. Another technique of impregnation is by an exact admixture of the components and a thorough pysical dispersion of the same; this may be carried out by placing the requisite amount of moist cellulose, which may have been pretreated by swelling in alkali followed by washing and centrifuging or air drying to a suitable moisture content, into one of the types of mixer known in the viscose processing art (e.g. of the Werner-Pfleiderer type), adding to the cellulose the required amount of urea with or without additional water whilst the mixer is operated and adding the required amount of phosphorus acid in several small portions followed by further mixing until a substantially well dispersed mix is obtained. When powdered cellulosic material is to be treated it is preferred to mix the powder intimately with a sufficient quantity of liquor to ensure uniform distribution and then to remove the excess. The liquor is applied to the cellulosic material at room temperature or below, or at an elevated temperature.

The rate and degree of reaction between the cellulosic material and the liquor is affected by the pH of the liquor and preferably the pH is adjusted to between 2 and 7, for example by the addition of ammonium hydroxide.

After the impregnation of the cellulosic material with the liquor it is cured by heating at a temperature between 120° and 200°C., preferably between 125° and 150°C. The higher temperatures tend to produce charring. This curing is carried out for at least 20 minutes but normally for not more than 4 hours. Preferably the curing takes place in a well ventilated oven in which heated air or other gas e.g. nitrogen or a mixture containing ammonia, is passed through or over the material. Alternatively, the drying and curing may be carried out in a revolving perforated drum, on a travelling band or in a cyclone type dryer. Infra red heating may in some cases be used.

After curing, the product is desirably treated for the removal of water-soluble substances, e.g. by being placed in an excess of water and washed free of phosphates and other waer-soluble by-products. The product is preferably then dried by air drying or by drying in an oven at a temperature below 100°C. If desired the drying may be carried out in the presence of ammonia. The water may alternatively be removed by treatment with volatile solvents e.g. by washing with alcohol followed by treatment with ether, and evaporating off the ether.

In one form of the present invention the washing step is followed by a further step to convert the product to the hydrogen or a preferred salt form e.g. sodium or calcium form. This may be effected by commencing the washing procedure using water and then changing to a dilute acid to convert to the hydrogen form or a salt solution to convert to the appropriate salt form. The excess acid or salt solution is washed out. For instance to obtain a product in the sodium form, the phosphorylated cellulose is washed with water in the normal way and then given a further wash with a sodium chloride or other sodium salt solution.

The final product may take the form of thread, filament, web, sheet, film, pulp, floc or powder or may be in the form of a gel.

The phosphorus containing cellulosic materials preparted according to this invention are believed to contain combined nitrogen, but this is not generally attached to the cellulose directly but is present as the ammonium or substituted ammonium salt of the phosphorus acid group. However, side reactions may produce traces of directly combined nitrogen, possibly as amide on a carboxyl group present.

Following is a description by way of example of methods of carrying the present invention into effect. The percentages employed throughout the specification are percentages by weight.

EXAMPLE 1

18 g. of ortho-phosphoric acid and 50 g. of

urea were dissolved in 32 g. of warm deionised water. A sheet of wood pulp weighing 25 g. was immersed in this solution, and allowed to soak up all of the solution. The uniformly saturated sheet was then heated in a well ventilated oven for 1½ hours at 130°C. It was then plunged into 1 litre of deionised water, well macerated, and filtered through a Buchner funnel. The pulp was washed with about 4 litres of water, until the washings gave no test for phosphate, sucked dry, and heat dried in an oven at 80°C. until the residual moisture content was 20%. The product contained 10% phosphorus.

EXAMPLE 2

The procedure of Example 1 was followed except that the curing was carried out using infra-red heating (sheet temperature 150°C.) for 1 hour. The product contained 11% of phosphorus.

EXAMPLE 3

The procedure of Example 2 was followed employing a liquor consisting of 16 g. orthophosphoric acid, 45 g. urea and 64 g. deionised water. The product contained 8% of phosphorus.

EXAMPLE 4

20 g. aminoguanidine hydrogen carbonate

$$[(H_2N—NH—C(=NH_2)—NH_2)^{+}\ HCO_3^{-}]$$

and 18 g. of orthophosphoric acid were thoroughly mixed, after which 39 g. of urea were added. The mixture was warmed for about 5 minutes, cooled, and 32 g. of water and 5 g. of 0.88 ammonium hydroxide added. 26 g. of wood pulp was steeped in this solution, the latter being completely taken up by the cellulose. The thus-treated pulp was heated for 70 minutes at 125°C. in a well ventilated oven, the product being washed and dried as described in Example 1. The product contained 6% of phosphorus.

EXAMPLE 5

15 g. urea and 7 g. guanidine nitrate were dispersed in 21 g. of distilled water and 4 g. orthophosphoric acid were added. A sheet of wood pulp weighing 8 g. was steeped in this liquor and the pulp was then squeezed to remove excess liquor, the pulp to liquor ratio obtained being approximately 1:4.5. The steeped sheet was then cured for 155 minutes at a temperature of 130°C. in a well ventilated oven (about 5 changes of air per minute). The steeped sheet was then plunged into 1 l of deionised water, well macerated, and filtered through a Buchner funnel; the pulp was washed with about 4 l. of water until the washings gave no test for phosphate and then sucked dry. The product contained 7.3% of phosphorus, was white in colour and of good texture.

EXAMPLE 6

7 g. phenylbiguanide and 13 g. of urea were dissolved in 29 g. of water to which 4 g. of orthophosphoric acid were added. A sheet of wood pulp weighing about 7 g. was steeped in the above liquor and the pulp was then squeezed to remove excess liquor to give a pulp:liquor ratio of about 1:4. The sheet was cured in a well ventilated oven for 153 minutes at a temperature of 130°C. and then washed as described in Example 5. The product contained about 6% by weight of phosphorus and was white.

EXAMPLE 7

7.5 g. formamide were mixed with 5 g. urea, 4 g. ortho-phosphoric acid and 25 g. water. A sheet of cellulose was steeped in this liquor to obtain a pulp:liquor ratio of about 1:5. The sheet was cured for 140 minutes at a temperature between 125 and 130°C and then washed, as described in Example 5. The product contained 8.6% phosphorus and was white.

EXAMPLE 8

10 g. of each of orthophosphoric acid and ammonium dihydrogen phosphate were dissolved in 30 g. water, to which 20 g. of urea were added. After dissolving the urea a piece of wood pulp was steeped in this liquor to give a ratio of pulp:liquor of 1:4. This was cured in a well ventilated oven (with about 5 changes of air per minute) for 120 minutes at 130°C. and then washed, as described in Example 5. The white product contained 10.5% phosphorus.

EXAMPLE 9

A solution was prepared from 5 g. of guanyl urea sulphate, 10 g. urea, 7 g. orthophosphoric acid, and 26 g. water. In this liquor a sheet of wood pulp was steeped to give a pulp to liquor ratio of 1:4.5. This was heated for 100 minutes at 130°C. in a well ventilated oven (about five changes of air per minute), and then washed, as described in Example 5. The product contained 7.3% phosphorus.

EXAMPLE 10

25 g. urea were dissolved in 18 g. water to which 16 g. metaphosphoric acid were added. This liquor was used for steeping a sheet of cellulose to a pulp to liquor ratio of about 1:3.5. On curing for 120 minutes at 130°C. and washing, as described in Example 5, a phosphorus content of about 11% was obtained in the white product.

EXAMPLE 11

16 g. phosphorus acid, 50 g. urea and 30 g. water were mixed to obtain a liquor in which about 10 g. sheeted wood pulp were steeped. The pulp was then squeezed to remove excess liquor and to produce a material having a pulp to liquor ratio of about 1:3.7. On curing this for 60 minutes at 130°C. in a well ventilated oven and after washing, as described in Example 5, a product having a phosphorus content of 7.8% was obtained. The product had cation exchange properties, was almost white in colour and was in the form of a gel. A similar product could be obtained by

decreasing the urea content of the liquor to 30 g. from 50 g. used in this example.

EXAMPLE 12

16 g. urea phosphate, 6 g. urea, 10 g. ammonia (0.88) and 29 g. water were made up into a liquor which was used to steep cellulose to a pulp to liquor ratio of 1:4. This was heated at 125° to 130°C. for 2 hours and then washed, as described in Example 5; the product obtained contained 9.5% phosphorus and was white in colour.

EXAMPLE 13

20 g. urea were dissolved in 30 g. water and 10 g. ammonium dihydrogen phosphate were added. When the latter dissolved the liquor was used for a preparation similar to those quoted above where the steeped cellulose was heated for 2 hours at between 125° and 130°C., the pulp to liquor ratio being 1:3.7. The phosphorus content of the washed product given thereby was 9.6%. The product was white.

EXAMPLE 14

This example illustrates the effect of curing time upon the phosphorus content of the product.

The liquor used for treating the wood pulp consisted of ortho-phosphoric acid 18.4%, urea 49.6% and distilled water 32%. The pulp to liquor ratio was 1:3 and the temperature of curing was 130°C.

When the curing time was 75 minutes, the phosphorus content of the washed product was 8.7%. When the curing time was 105 minutes, the phosphorus content of the washed product was 10.3% and when the curing time was 135 minutes, the phosphorus content was 10.9%.

In each case the curing was carried out in a well ventilated oven with about 4 changes of air per minute.

EXAMPLE 15

This example illustrates the effect of a change in the pulp to liquor ratio on the phosphorus content of the product, the composition of the liquor, the nature of the cellulosic material and the curing temperature being that stated in Example 14 and the time of curing being 135 minutes.

When the pulp to liquor ratio was 1:4 the phosphorus content of the washed product was 11.5%, when the pulp to liquor ratio was 1:3 the phosphorus content of the washed product was 10.9%. The curing was carried out in a well ventilated oven in each case with about 4 changes of air per minute.

EXAMPLE 16

This example illustrates the influence of the temperature of curing on the phosphorus content of the cellulose product when made with the cellulose pulp and liquor of Example 14, a pulp to liquor ratio of 1:3 and a curing time of 50 minutes.

When the temperature of curing was 130°C. the phosphorus content of the washed product was 9.2% and when the temperature of curing was 140°C. the phosphorus content was 10.6%.

In this example six changes of air per minute were used in the curing oven.

EXAMPLE 17

This example illustrates the effect of employing different forms of cellulose. The liquor composition and temperature of curing were those employed in Example 14, the pulp to liquor ratio was 1:4.5, and the time of curing was 150 minutes.

When wood pulp was used under these conditions the phosphorus content of the washed product was 14% and when cotton pulp was employed the phosphorus content was 9%.

EXAMPLE 18

This example illustrates the effect of variation of the air flow during the curing operation on the phosphorus content of the washed product.

The pulp and liquor used, the pulp to liquor ratio and the temperature of curing were those of Example 14. The time of curing was 150 minutes.

When the curing was carried out with 16 changes of air per minute, the phosphorus content of the product was 11.8%. With 11 changes of air per minute the phosphorus content was 12% and with 6 changes of air per minute the phosphorus content was 11%.

EXAMPLE 19

This example illustrates the effect of the addition of ammonia to the liquor on the phosphorus content of the product.

The pulp and liquor employed and the temperature of curing were those stated in Example 14. The pulp to liquor ratio was 1:4.7 and the time of curing was 150 minutes. When no ammonia was added, the phosphorus content of the resulting washed product was 13%. When about 14% of 0.88 ammonium hydroxide was added, resulting in a liquor having a pH of about 4, the phosphorus content of the washed product was 11.5%.

EXAMPLE 20

The effect on the phosphorus content of the product of using a gas other than air in the curing operation is illustrated in this example in which the pulp and liquor employed, the pulp to liquor ratio and the temperature of curing were those mentioned in Example 14 and the time of curing was 50 minutes. Curing with 3 changes of atmosphere per minute, the employment of nitrogen resulted in a washed product having a phosphorus content of 11.6% and the employment of air resulted in a washed product having a phosphorus content of 11.5%.

EXAMPLE 21

The change in phosphorus content of the product resulting from changes in the composition of the liquor is illustrated in this example in which the pulp employed and the

temperature of curing was that of Example 14, the pulp t liquor ratio was 1 to 4.7 and curing was carried out with 2 changes of air per minute.

(a) Using a liquor of the composition of that used in Example 14 and a curing time of 180 minutes, the phosphorus content of the washed product was 15%.

(b) Using a liquor consisting of

18% orthophosphoric acid
25% urea
57% distilled water

and a curing time of 180 minutes, the phosphorus content of the washed product was 9%.

(c) Using 50% of a liquor as described in Example 14 with 50% of distilled water and curing for 160 minutes, the washed product had a phosphorus content of 9.2%.

EXAMPLE 22

100 g. of a high quality pure wood pulp is treated with 1 litre of 17.5% sodium hydroxide for 15 minutes. It is then diluted and the mixture transferred to a centrifuge where it is well washed with water. The pulp is then left in 6 litres of deionised water for 24 hours and again centrifuged and well washed. It is finally centrifuged down to a condition in which it contains 55% of water. From this it is possible to calculate the quantities necessary for the process which follows, namely 102.5 grms of this swollen pulp requires 124 grms of urea and 75 grms of water. This is placed in a mixing machine and thoroughly homogenized. This is followed by the addition of 29.4 mls of orthophosphoric acid (89%) and further mixing. The mixture is then transferred to a rotating perforated drum and heated at 130°C. for 170 minutes. The product is washed and dried in the usual manner and contains 13.6% of phosphorus.

EXAMPLE 23

Wood pulp weighing 200 grms is thoroughly steeped in 4000 grms of liquor (composition as example 14) after which it is centrifuged to a total weight of 1000 grms. The impregnated pulp is then subdivided into small particles which are transferred to a perforated rotating drum or a constantly agitated tray and heated at 130°C. for 150 minutes in a circulating draught of air. The product is washed with water followed by a wash with 5% sodium chloride solution and the excess salt solution subsequently removed by a further washing with water.

In the above examples the wood pulp employed contained approximately 8% moisture.

WHAT WE CLAIM IS:—

1. A process for the preparation of a phosphorus containing cellulosic material having selective adsorbent or ion-exchange properties, which process consists essentially in the impregnation of cellulosic material with an aqueous solution f a phosphorus acid and urea, the aqueous solution containing a relative proportion of nitrogen to phosphorus of at least one atom of nitrogen per atom of phosphorus, the ratio by weight of the solution t cellulose being at least 1.5:1 and the ratio by weight of cellulose to phosphorus acid in the reaction mixture not exceeding 5:1, and heating the impregnated material for at least 20 minutes at a temperature between 120° and 200°C., the heating of the impregnated material being such that the final product contains at least 5.5% by weight of combined phosphorus.

2. A process as claimed in claim 1 wherein the cellulosic material is wood cellulose in web, sheet, pulp, floc or powder form.

3. A process as claimed in claim 1 wherein the cellulosic material is cotton cellulose in thread, web, sheet, pulp, floc or powder form.

4. A process as claimed in claim 1, wherein the cellulosic material is regenerated cellulose in filament, film, web, powder, yarn or sheet form.

5. A process as claimed in any one of the preceding claims wherein the phosphorus acid is ortho phosphoric acid.

6. A process as claimed in any one of the preceding claims wherein the solution used to impregnate the cellulosic material consists of from 5 to 20 per cent by weight of ortho phosphoric acid, 10 to 50 per cent by weight of urea and 30 to 85 per cent by weight of water.

7. A process as claimed in any one of claims 1 to 3 wherein the solution used to impregnate the cellulosic material is a solution of urea phosphate.

8. A process as claimed in any one of the preceding claims wherein the cellulosic material is in sheet form and is impregnated by steeping it in the phosphorus acid liquor and thereafter removing any excess liquor.

9. A process as claimed in any one of the preceding claims wherein the impregnating solution has a pH adjusted to between 2 to 7.

10. A process as claimed in any one of the preceding claims wherein the impregnated material is cured by heating for between 20 minutes and 4 hours at a temperature of from 125° to 150°C.

11. A process as claimed in claim 10 wherein a gas is passed over or through the impregnated material during the curing.

12. A process as claimed in claim 11 wherein the gas is air.

13. A process as claimed in claim 11 wherein the gas is nitrogen.

14. A process as claimed in any one of the preceding claims wherein after curing the product is placed in an excess of water and washed free of phosphate and other water-soluble by-products, the product being subsequently dried at a temperature below 100°C.

15. A process as claimed in any one of the preceding claims wherein after curing the

product is converted to the hydrogen or a salt form by washing with a dilute acid or a salt solution respectively.

16. A process as claimed in any one of the preceding claims wherein the product is dried by treatment with volatile solvent.

17. A process as claimed in claim 16 wherein the product is dried by treatment with alcohol followed by treatment with ether and evaporating off the ether.

18. A process for the preparation of a phosphorus-containing cellulosic material substantially as described in any one of the specific examples hereinbefore set forth.

19. Phosphorus-containing cellulosic material whenever prepared by a process as claimed in any one of the preceding claims.

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PROVISIONAL SPECIFICATION

Improvements in or relating to Cellulosic Material

We, W. & R. BALSTON LIMITED, a British Company, of Springfield Mill, Maidstone, Kent, do hereby declare this invention to be described in the following statement:—

This invention is for improvements in or relating to cellulosic maerial and is particularly concerned with the preparation of phosphorus-containing cellulosic material.

It is an object of the present invention to prepare a phosphorus-containing fibrous cellulosic material having selective adsorbent or ion-exchange properties for the purpose of separating mixtures by preferential selection, *e.g.* by chromatographic methods.

According to the present invention there is provided a process for the preparation of a phosphorus-containing cellulosic material which process comprises impregnating the cellulosic material with an aqueous solution of a phosphorus acid and a basic nitrogen-containing compound or an aqueous solution of a compound of a phosphorus acid and a basic nitrogen-containing compound, the relative proportion of nitrogen to phosphorus in the mixture or in the compound being at least one atom of nitrogen per atom of phosphorus and the ratio of the solution to cellulose being at least 1.5 to 1, heating the impregnated material for at least 20 minutes at a temperature between 100° and 200°C. and thereafter treating the material for the removal of water-soluble substances and drying.

The cellulosic material which is treated in accordance with the present invention is fibrous cellulose of various origins, such as wood cellulose and cotton cellulose, and it may be in web, sheet, pulp or powder form.

The treated cellulose contains at least 5.5% phosphorus and this is achieved by employing a liquor to cellulose ratio of at least 1.5:1, the liquor present in the cellulose after the impregnation step being such that the cellulose contains sufficient phosphoric acid to be capable of yielding a product containing not less than one combined phosphate group for every three monosaccharide units of the cellulose.

In a preferred form of the present invention the solution used to impregnate the cellulosic material consists of,

Orthophosphoric acid	5 to 20% by weight
Urea	10 to 50% by weight
Water	to make up to 100%.

In some forms of the present invention up to 25% by weight of orthophosphoric acid may be employed, and in others up to 60% by weight of urea. The ratio of urea to phosphoric acid must be greater than 1.5:1.

Other phosphorus acids, *e.g.* phosphorous acids, may be employed in place of orthophosphoric acid. Examples of other basic nitrogen-containing compounds include biuret, acetamide, formamide, guanidine, aminoguanidine, biguanidine, and guanylurea.

Examples of suitable compounds of phorphorus acids and nitrogen-containing compounds which may be employed in aqueous solution in one form of the present invention are ammonium phosphate, dimethylamine phosphate, propylamine phosphate, urea phosphate, guanylurea phosphate and aminoguanidine phosphate.

The aqueous solution of the acid and nitrogen-containing compound may be prepared by dissolving the two compounds in hot or cold water or by melting the two compounds together and then dissolving the hot or cooled melt in water.

The impregnation of the cellulosic material is carried out by steeping it in the phosphorus acid liquor. The liquor is applied to the cellulosic material at room temperature or below, or at an elevated temperature.

The rate and degree of reaction between the cellulosic material and the liquor are effected by the pH of the liquor and preferably the pH is adjusted to between 2 and 7.

After the impregnation of the cellulosic material with the phosphoric acid/urea liquor it is cured by heating at a temperature between 100° and 200°C. preferably between 120° and 160°C. This curing is carried out for at least 20 minutes but normally for not more than 4 hours.

After curing the product may be placed in a large excess of water and thoroughly washed free of phosphates and other water-soluble by-products. The product is then dried by air drying or by drying in an oven at a temperature below 100°C. If desired the

drying may be carried out in the presence of a chemical vapour, *e.g.* ammonia.

Following is a description by way of example of methods of carrying the present invention into effect.

EXAMPLE 1

18 g. of ortho-phosphoric acid and 50 g. of urea were dissolved in 32 g. of warm deionised water. A sheet of wood pulp weighing 25 g. was immersed in this solution, and allowed to soak up all of the solution. The uniformly saturated sheet was then heated in a well ventilated oven for 1½ hours at 130°C. It was then plunged into 1 l. of deionised water, well macerated, and filtered through a Buchner funnel. The pulp was washed with about 4 l. of water, until the washings gave no test for phosphate, sucked dry, and heat dried in an oven at 80°C. until the residual moisture content was 20%.

EXAMPLE 2

The procedure of Example 1 was followed except that the curing was carried out using infra-red heating (sheet temperatures 150°C.) for 1 hour.

EXAMPLE 3

The procedure of Example 2 was foll wed employing a liquor consisting of 16 g. orthophosphoric acid 45 g. urea and 64 g. deionised water.

EXAMPLE 4

20 g. aminoguanidine hydrogen carbonate and 18 g. of orthophosphoric acid were thoroughly mixed, after which 30 g of urea were added. The mixture was warmed for about 5 minutes, cooled, and 32 g. of water and 5 g. of 0.88 ammonium hydroxide added. 26 g. of wood pulp was steeped in this solution, the latter being completely taken up by the cellulose. The thus-treated pulp was heated for 70 minutes at 125°C. in a well ventilated oven, the product being washed and dried as described in Example 1.

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